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Preparation and characterization of fluoridated hydroxyapatite coatings on HT-C/C composites

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ABSTRACT

Monetite-like coatings were deposited from a solution containing Ca and P ions onto H_2O_2 treated Carbon/Carbon composites (HT-C/C) by ultrasonic induction heating (UIH) and subsequently subjected to ammonia hydrothermal treatment to form hydroxyapatite (HA). Subsequently, this HA coating was placed in a NaF solution and hydrothermally treated to produce fluorinated hydroxyapatite (FHA) coatings. The structure, morphology and chemical composition of the HA and FHA coatings were characterized by SEM, XRD, XPS, EDS and FTIR, and the adhesiveness and dissolution rate were examined by a scratch test and an immersion test respectively. The results showed that incorporation of F into HA led to an increase in the adhesiveness but a decrease in the dissolution rate of HA coating on C/C. With increasing hydrothermally fluoridation temperature, the F content in the FHA coatings increased and their dissolution rate decreased. However, the adhesiveness of these FHA coatings on C/C first increased from 42.7 N to 54.2 N as the hydrothermal fluoridation temperature increased from 353 K to 393 K, and then decreased to 18.3 N at 413 K. The reasons for changes in the adhesiveness and dissolution rate of the coatings were discussed.

1. Introduction

Carbon/carbon composites(C/C) possess excellent biocompatibility, high corrosion resistance, lightweight and good mechanical properties, and, in particular, their elastic modulus is similar to that of human bone. Therefore, they have been considered as implant materials in orthopaedic and dental prosthesis. However, they are biologically inert and thus cannot chemically bond to bone tissue. Also, C/C without surface modification often release carbon debris due to friction damage during surgical procedures, causing a blackening of the tissue [1,2]. Blackening is probably of no consequence. But, as the abraded carbon particles will be distributed throughout the body by the lymphatic system, they will end up eventually in the liver and may cause hepatic degeneration.

To overcome these shortcomings, during past decades, different bioactive coatings, such as bioactive glass, titanium dioxide and hydroxyapatite, etc., were prepared on C/C implants [3–5]. Among these coatings, HA has been the focus of considerable research because of its structural and compositional similarity to the mineralized matrix of natural bone. However, a current problem is that HA coatings are more soluble than expected in vivo or in vitro, which reduces the long-term stability of the coating [6]. In contrast to HA, fluorinated hydroxyapatite (FHA) exhibits significant dissolution-resistant property and comparable biocompatibility. Also, the presence of fluorine in HA can provide better apatite-like layer deposition and protein adsorption, improve alkaline phosphatase activity, and enhance the proliferation and differentiation of osteoblastic cells. Thus, FHA can better promote bone regeneration [7,8]. Therefore, it is being currently considered as an alternative coating material.

There are several different preparation methods used to generate FHA coating as reported in the literature including plasma spraying, pyrolysis, magnetron sputtering, pulsed laser depositions, sol–gel and electrophoresis [9,10]. However, all these technologies were conducted at high temperature or involved high-temperature post-treatment which deteriorates the coating's stability and its bioactivity. Generally, these methods are reported to be applied on Ti surfaces and few studies have been conducted on C/C substrates. In 2009, a combination of ultrasonic-electrodeposition and ion exchange, reported by Chuang Wang etc. [11], was applied to prepare FHA coatings on C/C composites. However, the adhesion strength of FHA coating on C/C was on average only 4.08 MPa, which is still poor and needs to be enhanced.

In our previous study, a NaOH hydrothermal treatment method was first applied to convert the ultrasonic induction heating (UIH) deposited monetite-like coating on $(NH_4)_2S_2O_8$ treated-C/C (NT-C/C) composite to HA coating. Then, this HA coating was further transformed into an FHA coating by hydrothermal post-treatment in a NaF solution. However, because the produced impurities such as calcium oxides resided in the FHA coating, the FHA coating on C/C had decreased adhesive strength (a critical load of 42.4 N) and showed no significant improvement in dissolution rate compared with HA coating [12]. In order to improve the performances of FHA coating on C/C by this

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novel technology, another solvent should be chosen for hydrothermally treating C/C with calcium phosphate coating. In this study, an ammonia solution was first chosen to hydrothermally transform UIH deposited monetite-like coating on C/C to HA coating, and then a NaF solution was applied to produce an FHA coating at different temperature. The composition, structure, morphology, mechanical and dissolution properties of the HA and FHA coatings were investigated.

2. Materials and methods

Induction heating deposition (IHD) was performed using an SP-15 high frequency induction heater (Shenzhen SuanPin Power Co. Ltd). The experimental setup was described elsewhere [13]. In this experiment, the IHD process was performed in an ultrasonic bath with a power of 150 W and a frequency of 20 kHz. The solution of 0.08 M Ca and 0.048 M P ions used in this study was prepared by dissolving reagent-grade $Ca(NO_3)_2$ and $NH_4H_2PO_4$ in distilled water.

Small specimens of C/C composites (Diameter 12 mm × 10 mm) were cut from bulk 3D materials with a density of about 1.80 g/cm^3 produced by Central South University. These specimens were pretreated in high pressure steam at 160 °C with 40 ml 2 M H_2O_2 in a 50 ml autoclave. The specimens were then ultrasonically rinsed with deionized water and dried in air.

All deposition experiments were carried out at an applied current of 450 A at room temperature for 20 min. At the end of each run, the coated samples were rinsed with distilled water and then immersed in a 20% ammonia solution for hydrothermal treatment at 140 °C for 4 h in a 50 ml autoclave. After the first-step hydrothermal treatment, all coated samples were hydrothermally treated in an autoclave with 40 ml NaF solutions of 0.01 M at temperatures of 353 K and 413 K for 24 h. Ultimately, the as-prepared specimens were washed with deionized water in an ultrasonic bath and then annealed in vacuum at 200 °C for 1 h to remove the water in the coatings.

The chemical states of the atoms in the pretreated C/C composites were investigated by X-ray photoelectron spectroscopy (XPS; ULVAC-PHI 1800, Japan) with an Al Kα X-ray source (1486.6 eV). Prior to XPS measurement, each sample was etched using an argon gun with its energy being 4 keV, current equal to 1 μA and the erosion time close to 1200 s. The crystalline structure, morphology and composition of the coated samples were characterized by a D8 Advance X-ray diffractometer (Cu-Ka radiation), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis with an s-3400N (Japan) microscope. The functional groups of the HA coatings were identified by Fourier transform infrared (FTIR) in the 400–4000 cm^{-1} range with a resolution of 4 cm^{-1} using a Perkin Elmer Instruments Spectrum One Spectrometer and KBr pellet technology. The bonding strength of the HA and FHA coatings deposited on C/C substrates was determined by an s-3400N scratch tester fitted with a Rockwell C 0.2 mm-diamond stylus with a preload of 1 N. The load speed, maximum load and scratch speed were 35 N/min, 70 N and 2.5 mm/min respectively. The created scratch was studied with an optical microscope to obtain the critical load at which the coating detached from the C/C substrate and thus determine the critical pressure. Finally, the scratch trace of the HA and FHA coatings was observed by a stereomicroscope (SM).

The dissolution rate of the HA and FHA coatings was measured in physiological saline solution (0.9% NaCl). After these samples were immersed for pre-determined time periods, a 10 ml immersion solution was extracted and the dissolved Ca ion concentration was measured by means of inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 2100 DV, Perkin Elmer, American).

3. Results and discussion

The XRD patterns of HT-C/C, the deposited and post-hydrothermal treated coatings on HT-C/C are shown in Fig. 1. The coating deposited by induction heating method consisted of $CaHPO_4$ (monetite-like) (Fig. 1(b)). After ammonia hydrothermal post-treatment, monetite-like was transformed to hydroxyapatite (Fig. 1(c)) identified by the three most intensive peaks ((211), (300), (112)) between 2θ = 30–35º [14]. After further hydrothermal treatment in NaF solution at different temperatures, the XRD peaks of the coatings did not shift compared with those of HA coatings, as shown in Fig. 1(d)–(g). Generally, the (300) peak position of FHA will slightly be shifted to a higher diffraction angle compared with that of HA coating because the a-axis parameter in HA crystal is reduced by incorporation of F^- into the apatite structure [15]. However, in our study, these phenomena were not found.

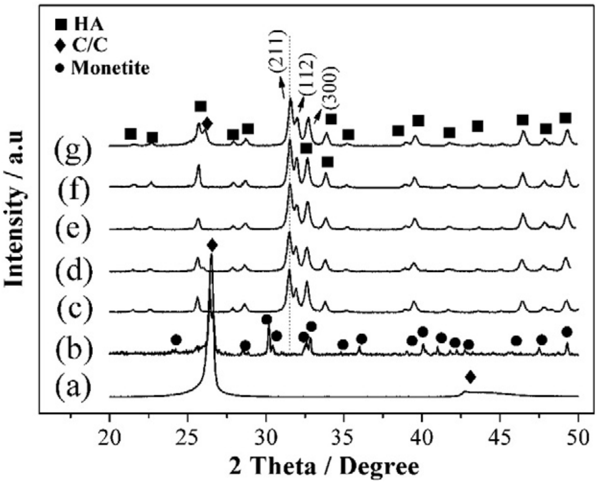

Fig. 1. XRD patterns of (a)NT-C/C, (b) UIH deposited monetite-like coating, on HT-C/C and as-transformed HA coating (c) by ammonia hydrothermal treatment and as-prepared FHA coatings at (d) 353 K, (e) 373 K, (f) 393 K and (g) 413 K respectively by ammonia and subsequently NaF solution hydrothermal post-treatments.

To determine whether F ions were incorporated into HA lattice, XPS was performed on HA and FHA coatings as shown in Fig. 2(a) and (b). From Fig. 2(a), it can be observed that after hydrothermal fluoridation treatment, F1s peaks occurred in the patterns, and with increasing temperature, the intensities of these peaks increased. Further narrow scan analysis, as given in Fig. 2(b) reveals that this F1s peak was positioned at 684.3 eV. According to Ref. [16], the peak at 684.3 eV is the fingerprint for fluorine in FHA structures, and thus it can be deduced that F ions have been incorporated into HA coatings on HT-C/C. Additionally, there was a small Na1s at 1072.0 eV, which was attributed to HA not to NaF (Na1s at 1071.2 eV) [17]. This means that Na ions were also incorporated into apatite lattice.

The surface chemical compositions of the coatings were also analyzed by XPS and EDS, and the results are shown in Table 1. It can be seen that the as-deposited monetite-like coating shows a Ca/P atomic ratio of 1.18, larger than the stoichiometric ratio of monetite, which might correlate with the ultrasonic cavitation effect [12]. When an ultrasonic wave passes through a solution, many microbubbles will be generated which on subsequent collapse form many cavities. The temperature within cavities can reach values as high as 3400–4300 °C [18]. This temperature is sufficient to thermally decompose monetite causing a loss of P_2O_5. Hence the resulting coating shows a Ca/P ratio larger than 1. After the ammonia hydrothermal treatment, the as-achieved HA showed a Ca/P atomic ratio of 1.80 which was larger than the theoretical ratio of HA (1.67). If from the Ca/P atomic ratio of the as-achieved HA the value (1.67) of stoichiometric hydroxyapatite is subtracted, then 0.13 will be obtained. This value is close to 0.18, the difference of the Ca/P atomic ratio of the as-deposited monetite-like and that of stoichiometric monetite-like. So, it can be inferred that the excess Ca/P ratio of the HA coating on HT-C/C originated from the monetite-like coating deposited by UIH